



Article

Activation of the Fuels with Low Reactivity Using the High-Power Laser Pulses

Roman I. Egorov ^{1,†} , Alexandr S. Zaitsev ^{1,†} and Eugene A. Salgansky ^{2,*,†} 

¹ National Research Tomsk Polytechnic University, 30 Lenin Avenue, 634050 Tomsk, Russia; rommel@tpu.ru (R.I.E.); alexzaitsev@tpu.ru (A.S.Z.)

² Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 Acad. Semenov Avenue, 142432 Chernogolovka, Russia

* Correspondence: sea@icp.ac.ru; Tel.: +7-496-522-1368

† These authors contributed equally to this work.

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Abstract: In this paper we have proposed the simple and effective approach to activation of the low reactivity industrial fuel which can be used immediately inside the furnace. The high-power laser pulses initiates partial gasification of the fuel together with its ultra-fine atomization. The gas-aerosol cloud surrounding the initial coal-water slurry droplet can consist of approximately 10% (after absorption of hundred pulses) of the initial droplet weight. The ratio of the syngas and aerosol weights is like 1:2 when pulse intensity is higher than 8 J/cm². The size and velocity distributions of the ultra-fine aerosol particles were analysed using the original realization of the particle tracking velocimetry technique.

Keywords: fuel activation; waste-derived fuel; coal-water slurry; laser pulse; syngas; aerosol

1. Introduction

An ignition delay time is one of the most important parameters of industrial fuels which makes direct influence onto the design of the furnaces. Numerous investigations are targeted on the optimization of the ignition of industrial fuels [1,2]. Decreasing the ignition delay time of the popular fuels, one can make a step to the smaller heaters or to an essential simplification of the ignition process [3]. This, in turn, will decrease the price of heaters and, therefore, the final price of the heat.

There are some different approaches for ignition optimization: switching to more appropriate temperatures by the usage of the furnace pre-heating and/or fuel activation by different ways (using the finer fuel atomization or introduction of special additions which simplifies an ignition, etc). All mentioned techniques have own benefits and weak points and can be used together for the best effect.

However, most of the ignition-related problems become much sharper when used the cheap waste-derived fuels [4]. Such fuels typically have the very low level of the reactivity at the low temperatures [5]. This automatically requires higher furnace temperatures for a stable ignition. However, even in this case, the too long ignition delay time can make them non-appropriate for most of the existing boilers. There are two real ways for fuel adaptation: decreasing of the fuel particle size during atomization and addition of any ignition stimulating chemicals. Both of these ways have limitations (rheological or commercial) for traditional approaches [6,7]. Therefore, the simple method allowing the fuel activation with minimal changes of the furnace design will be always of interest. It is clear too, that the most effective way should include complex influence on the fuel. Methods combining the finer atomization together with pre-heating, intensification of the volatiles release or fuel gasification are always of interest.

In this paper we suggest the new approach to the pre-ignition processing of the fuel droplets by the high-power laser pulses [8–10]. This leads to two main effects *combined altogether*: from the one hand, laser pulse initiates an additional fine atomization of the fuel droplet. From the other hand, it leads to partial gasification [11–13] of the fuel, producing the cloud of combustible gas around the initially injected fuel droplet. Both these effects transform certain part of the fuel matter into the highly reactive state (micrometer scale particles and volatiles have much lower ignition delays times). The numerous investigations about ignition of different fuels [14–16] make a proof that increasing the volatiles release rate together with increase of the atomization quality always stimulate an ignition. In principle, the proposed method can work with different types of non-transparent liquid or solid fuels. An activation occurs due to mechanical and thermal effect of light pulses and, therefore, it is independent enough of its wavelength.

The proposed approach can be applied immediately inside the furnace and it means that the fuel activation will occur before ignition. That is the fuel can be stored for a long term in natural low reactivity state satisfying the fire safety requirements. The light-induced fuel activation does not require any modification of the chemical content of the fuel as well as expensive modifications of the fuel injection systems. All what is needed is a small side hole for laser beam input.

2. Materials and Methods

We have prepared the fuel composition with low reactivity whose ignition parameters are more or less clear at this moment from the previous investigations [1,17]. The waste-derived coal-water slurry (CWS) was made of the filter cake of fiery coal (particle size $\sim 140 \mu$) [17]. The water content of the slurry was ~ 40 wt %. The coal powder shows strong *hydrophilic* behaviour. The static contact angle of water droplet on the surface of the pressed dry filter cake is $\sim 130^\circ$ (measured by the sessile droplet method [18,19]). The powder mixed with water form a slurry which looks like a black viscous substance (density $1.5\text{--}1.54 \text{ kg/m}^3$, viscosity $10\text{--}15 \text{ mPa}\cdot\text{s}$) which can absorb most part of an incident light of visible range.

The surface structure of the coal particles (in the dry state pores contain up to 30 wt % of bound volatiles) as well as a lot of flocculants on the particle surface (introduced during the coal enrichment by floatation) determine the very good adhesion between the solid and liquid components of the slurry. Thus, there is not essential natural separation of the liquid and solid components before the fuel atomization. We have analysed the effect of laser pulses using the single fuel droplet fixed by the special holder under the laser irradiation.

Each laser pulse ($\lambda = 533 \text{ nm}$, pulse duration $\sim 10 \text{ ns}$, light intensity inside the spot $E_{\text{spot}} = 12 \text{ J/cm}^2$, pulse repetition rate 2.5 Hz) causes the micro-explosions on the surface of slurry droplet ($d \sim 2 \text{ mm}$). Thus, the solid slurry matter partially ablates [8,9] as well as some of water evaporates after the pulse came. Additionally, some of the matter fly out of the sample surface in the form of ejected micro droplets. The experimental setup is shown in Figure 1.

The CW-laser (power is 300 mW at 533 nm) was used for illumination of the flow of micro explosion products by the astigmatic beam having $\sim 10^\circ$ angle with the propagation direction of the pulsed beam. The illuminated particles, flying in the plane of the CW-beam, are observed by the high-speed video camera Phantom V411 ($800 \times 600 \text{ px.}$ and $10,000 \text{ fps}$) with macro optics. This realization of the particle tracking velocimetry technique [20,21] allows easy gathering of the particle size and velocity distributions as well as visualization of the trajectory of gas/aerosol cloud. The overall spatial resolution of the PTV system was at the level of $7 \mu\text{m}$.

The corresponding changes in the sample weight are measured by the analytic balances Vibra AF 225DRCE. The sample droplet of the slurry was placed on the plate of the balances specially for monitoring of the gasification efficiency. The chemical composition of the atmosphere inside the reaction volume was analysed by the gas analyser Boner Test-1 adapted for measurements of the low concentrations of gases.

Usually we recorded fifty videos showing interaction of light pulses with a fuel to accumulate the statistics for size and velocity distributions of the aerosol particles. All measurements (including the control of weights of atomized matter and syngas chemical content) were repeated three times to avoid the influence of any random factors on the results. The statistical distributions, typical travel distances for aerosol cloud, syngas weights and concentrations show the variation of key values for less than 5%.

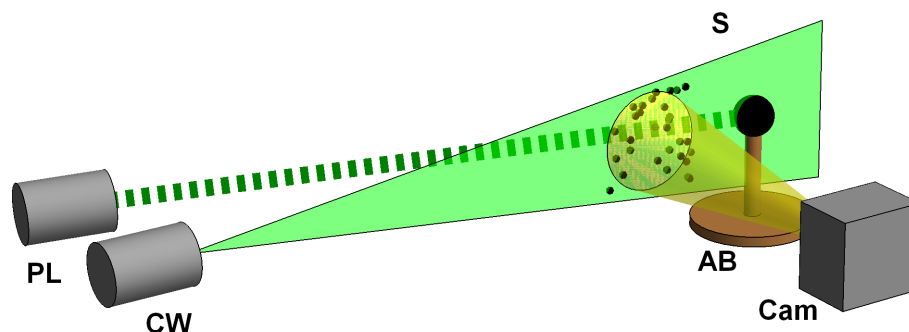


Figure 1. Scheme of the experimental setup including the nanosecond pulsed laser (PL), CW-laser (CW), analytic balances platform (AB), high-speed camera (Cam), sample of the fuel (S).

3. Interaction of The Laser Pulse with Slurry Fuel

An interaction of the focused light with matter can occur by two principally different ways. The continuous wave light absorbed by the sample surface trivially heats the sample gradually increasing its temperature with time. The high-power laser pulses interact with a matter by another way. In this work, we sent the 10 ns pulses with 100 mJ energy toward the sample surface (an illuminated area with radius like 0.5 mm). Each pulse causes the micro explosion on the fuel surface producing the ejection of micro particles (both water droplets and wet coal). The cloud of these particles propagates along the pulse path in backward direction with a certain transverse dispersion. The video of this process is shown in Supplementary Materials.

As one can see there are two types of objects: the sharp fast spots are mentioned ejected particles and the slow diffuse spots are the clouds of gasified volatiles. The high-power nanosecond pulse increases the temperature on the surface of coal particle up to 2000–2500 K [22,23]. Of course, such extreme state has a duration comparable with a pulse duration with further fast cooling. The depth of an extremal heating is like some micrometers. Therefore, the small part of the matter is ablated producing the mixture of the water steam and gaseous oxides of solid part of the fuel. The chemical content of the used filter cake (as well as for most of coals) allows effective production of CO, SO₂, different nitrogen oxides and a little of methane. The CO₂ usually is absent when coal particles are wet as it is shown in our previous investigations [11,12]. The massive release of water steam from the fuel sample simultaneously with carbon ablation leads to decrease of the partial pressure of oxygen near the place of carbon evaporation. This, in turn, suppresses the production of the CO₂. However, the contribution of water is much wider. When the temperature on the surface of coal particle overcomes the certain value (typically it have to be approx. 1000 K or higher) water starts the partial oxidation of carbon according to reaction: $H_2O + C \rightarrow H_2 + CO$.

It worth to note, that typical CWS contains less than 50 wt % of water (due to the rheological requirements [4,15]) and, thus, this reaction goes in our case with an evident deficit of water. It explains the fact that production of hydrogen is one order magnitude less than production of CO (which has an additional channel of production due to the carbon oxidation by the oxygen from air).

The Figure 2b–d shows some video frames with propagating gas-aerosol cloud which correspond to some moments after pulse-fuel interaction. As one can see, the quasi-straightforward propagation of the cloud occurs during approx. 4–4.5 ms. After this time the center of mass of an ejected matter cloud almost stops at approximately 1 cm distance from the initial fuel portion. Further evolution of gas-aerosol cloud is a trivial diffusion in all around direction with slow decrease of volume

concentration. Of course, this experiment is done in a steady state atmosphere whereas the realistic case is a fuel droplet flying in hot furnace. However, this simple case demonstrates the processes going around the fuel droplet under the effect of the laser pulses.

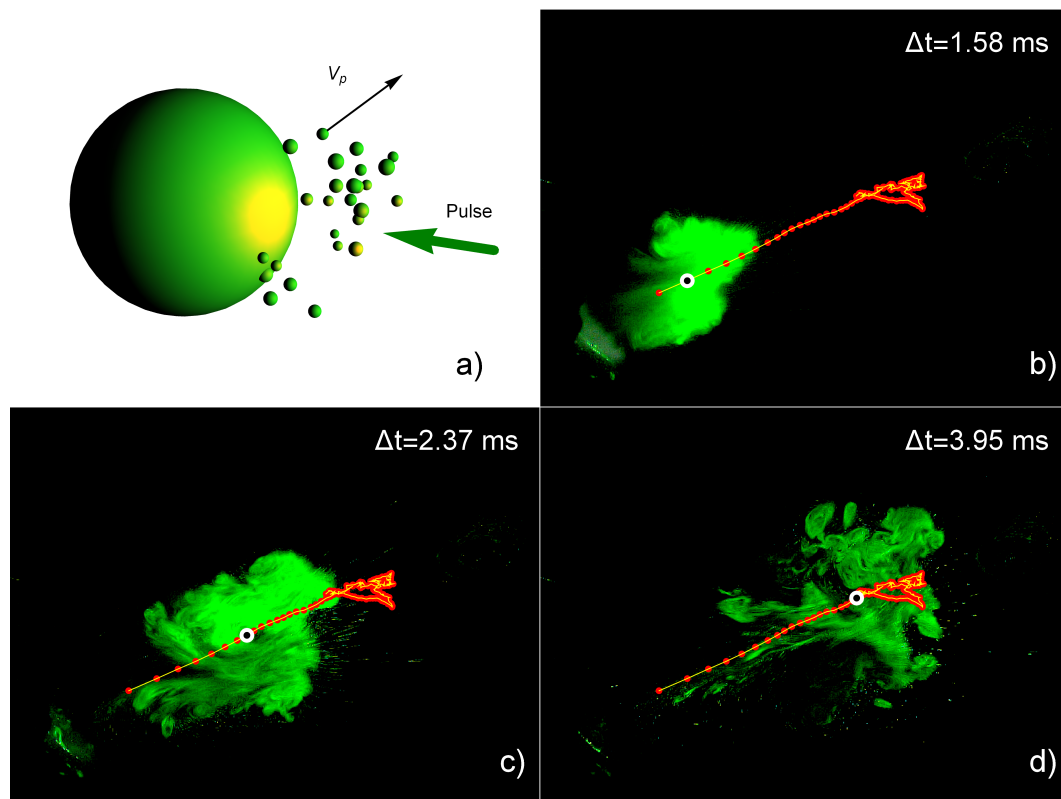


Figure 2. An interaction of the light pulse with an initial fuel droplet (a). The sequence of video frames showing the propagation of the gas-aerosol cloud (b–d). The green diffuse spot is a gas cloud, small green spots are ejected particles. The trajectory of the center of mass of cloud is shown by yellow line with red points (its position at moment Δt is marked by the white ring).

The repetition rate of laser pulses was low enough to observe the effect of the single pulse. Typically the cloud was observable during less than 20 ms which is much less than inter-pulse time gap. However, the long series of pulses lead to an increase of the residual concentration of the finely atomized fuel around the initial droplet. As result, the cloud decay time increases up to 50 ms after absorption of 20–25 pulses in a row.

An estimation of the weight of the fuel which is typically atomized by the pulsed laser processing was done through monitoring of the weight of initial fuel droplet under the laser irradiation. The difference between initial and current weight of the droplet is an equal to the weight of finely atomized matter. This includes both the syngas and fuel aerosol. The production of an atomized matter with absorption of the laser pulses shown in Figure 3a. As one can see, the amount of ejected matter grows almost linearly with number of absorbed pulses. It achieves approximately 5% of initial fuel weight after hundred of the pulses when pulse intensity exceeds 8 J/cm^2 . An evident gap between the curves corresponding to 7.9 J/cm^2 and higher intensity corresponds to contribution of the gasification. The Figure 3b shows the changes of the CO production with increase of the laser pulse intensity. The 8 J/cm^2 looks as an evident threshold value when an effective gasification starts. The CO is a main component of the syngas which appears under the effect of the high-power light flow [11,12].

Therefore, we can estimate that the ratio between the syngas and fuel aerosol is not so far from 1:2. This means that approximately 2 wt % of an initial fuel droplet transforms to the syngas after absorption of hundred of laser pulses as well as 4 wt % becomes the aerosol particles.

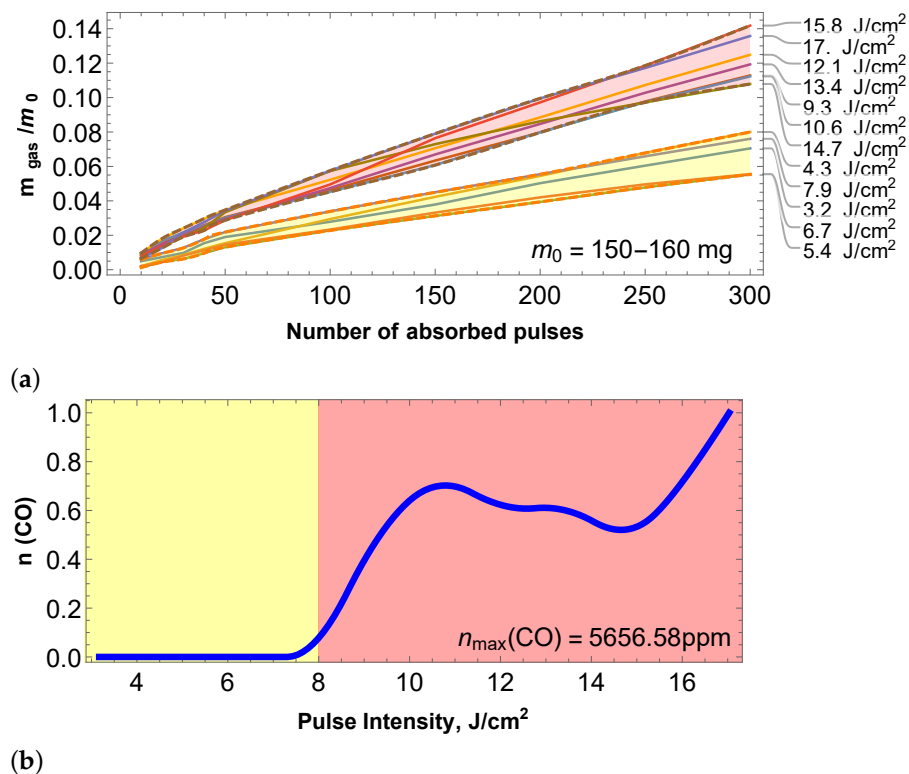


Figure 3. The dynamics of production of the finely atomized fuel under the effect of the laser pulses for different intensities (a). The dependence of the CO (main combustible component of the syngas) production efficiency (b) on the pulse intensity. The background in (b) shows the light intensity ranges below the threshold of an effective CO production (yellow) and above it (red).

Thus, we can conclude that an accumulation of the finely dispersed fuel (together with produced syngas) occurs around the initial fuel droplet. Changing the pulse repetition rate, we can variate the density of the finely atomized fuel. Taking in account the maximal distance of the cloud propagation, we can say that laser pulse processing effectively transforms each initial fuel droplet to a sphere (in steady state atmosphere) with 1 cm radius filled by a mixture of syngas, microscopic particles of coal and air. It is evident, that such objects are much better for a low-temperature ignition than an initial CWS droplets.

Parameters of the Obtained Aerosol

The dependence of ignition delay time on the droplet size for different types of the waste-derived coal-water slurry was analysed by Valiullin in [24,25]. It was shown that an ignition delay almost linearly decreases with fuel droplet size. The typical injection systems for industrial heaters allow fuel atomization to the average size like 1–5 mm. It corresponds to ignition delay times in range 3–15 s (at $T_{\text{furnace}} \sim 950\text{ K}$) that is much longer than for dry coal powder. Such delays make the CWS almost useless for heaters whose design is developed for coal dust which has much shorter ignition delays.

The laser pulse makes ultra-fine atomization of the fuel in comparison with effect of usual nozzles for highly viscous fuels. The particle tracking velocimetry approach [26,27] allows easy analysis of the dynamic properties of an ejected matter. The size and velocity distributions of the produced aerosol particles are shown in Figure 4. One can see, that most-probable size of the finely atomized fuel particles is less than $35\text{ }\mu\text{m}$. The most part of the produced aerosol particles have a sizes in range below $100\text{ }\mu\text{m}$. The maximal sizes observed during the experiments are up to $280\text{ }\mu\text{m}$. Such particle sizes are approximately one order of magnitude smaller than typically tested for ignition in numerous investigation. They potentially allow the ignition delay times in sub-second range for earlier mentioned furnace temperatures ($\sim 950\text{ K}$).

The Figure 4b shows the velocity distribution detected in aerosol flow going from the place of pulse impact. The most probable velocity is in narrow range above 0.1 m/s. The average velocity is approx. 1.1 m/s and the maximal one is up to 3 m/s. Thus, the aerosol cloud gets totally stopped the linear propagation in average after 10 ms.

Therefore, the pulse repetition rate can be increased for up to 100 Hz to speed up the fuel processing within the general approach developed in this paper. Such a way allows creation a very dense layer of the volatiles around the initial fuel particles. These volatiles together with ultra-fine aerosol potentially paves the way to ignition delays fully comparable with those that present for dry coal dust.

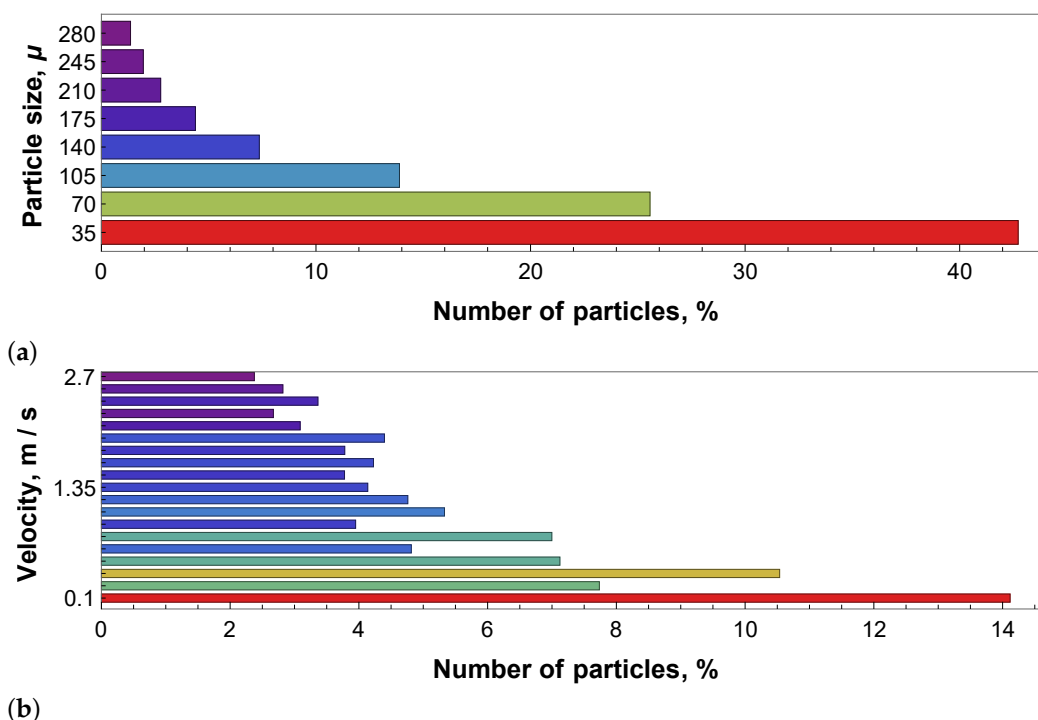


Figure 4. The size (a) and velocity (b) distribution of the finely atomized particles of the fuel aerosol.

Typically, the heterogeneous ignition of coal starts from the ignition of volatiles which are released during the coal heating. Our approach allows the fast conversion of 5–7 wt % of the CWS into the finely atomized form. Most of this are finely dispersed coal particles whose ignition delay time will be comparable with such parameter of volatiles. Increasing the repetition rate of the laser pulses we can increase the aerosol concentration for up to the order of magnitude using the commercially available laser modules. Additionally, the laser processing of the fuel inside the industrial systems can be realized as a propagation of the fuel particles through the sequence of parallel beams like in Figure 5. Such sequence can be cheap enough realized using the fiber-optics beam-splitters with one high-power laser module. Such a way gives a multiplication of the fuel atomization effect proportionally to the number of laser beams. Of course, different design of the laser processing stage can be successfully realized for different purposes. An application of the light pulses for an in-furnace fuel processing looks a convenient way for optimization of ignition and combustion of the low-reactivity fuels.

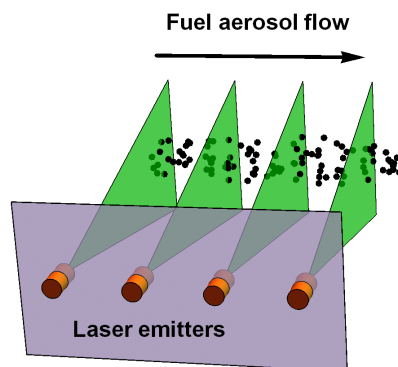


Figure 5. The sequential application of the laser processing for a flow of fuel aerosol from a usual injection nozzle.

4. Conclusions

We have proposed the simple technique that allows an effective increase of the amount of highly flammable fraction in the injected fuel flow inside a furnace. The high-power laser pulses interacting with injected CWS droplets with sizes that typically present in furnaces after injection nozzles allows formation of the ultra-fine fuel aerosol around initial droplets. Partial gasification of the coal by the light pulse makes an additional syngas shell which is fully similar to an addition of combustible volatiles. Typically, up to 5% of the droplet weight can be transformed to finely atomized state by nanosecond pulses with intensity like 8 J/cm^2 or higher.

Introduction of the aerosol and syngas clouds inside the furnace volume potentially allows essential acceleration of the fuel ignition. Physically it can work with different types of the solid or liquid fuels which optical density allows an effective absorption of the laser light.

The proposed approach can serve for in-furnace activation of the fuels which in general have the very low reactivity. Therefore, it can be the very practical way for adaptation of waste-derived fuels for the existing industrial furnaces.

In future we plan the detailed investigation of the physical basics of the observed processes. An influence of different factors like the fuel humidity onto the atomization properties as well as on syngas/aerosol ratio will be investigated.

Supplementary Materials: Supplementary materials are available online at <http://www.mdpi.com/1996-1073/11/11/3167/s1>.

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References

1. Bhuiyan, A.A.; Naser, J. CFD modelling of co-firing of biomass with coal under oxy-fuel combustion in a large scale power plant. *Fuel* **2015**, *159*, 150–168. [CrossRef]
2. Wang, X.; Niu, B.; Deng, S.; Liu, Y.; Tan, H. Optimization study on air distribution of an actual agriculture up-draft biomass gasification stove. *Energy Procedia* **2014**, *61*, 2335–2338. [CrossRef]
3. Tan, H.; Niu, Y.; Wang, X.; Xu, T.; Hui, S. Study of optimal pulverized coal concentration in a four-wall tangentially fired furnace. *Appl. Energy* **2011**, *88*, 1164–1168. [CrossRef]
4. Wang, Z.; Hong, C.; Xing, Y.; Li, Y.; Feng, L.; Jia, M. Combustion behaviors and kinetics of sewage sludge blended with pulverized coal: With and without catalysts. *Waste Manag.* **2018**, *74*, 288–296. [CrossRef] [PubMed]
5. Di Sarli, V.; Cammarota, F.; Salzano, E. Explosion parameters of wood chip-derived syngas in air. *J. Loss Prev. Process Ind.* **2014**, *32*, 399–403. [CrossRef]

6. He, T.; Chen, Z.; Zhu, L.; Zhang, Q. The influence of alcohol additives and EGR on the combustion and emission characteristics of diesel engine under high-load condition. *Appl. Therm. Eng.* **2018**, *140*, 363–372. [[CrossRef](#)]
7. Belal, H.; Han, C.W.; Gunduz, I.E.; Ortalan, V.; Son, S.F. Ignition and combustion behavior of mechanically activated Al–Mg particles in composite solid propellants. *Combust. Flame* **2018**, *194*, 410–418. [[CrossRef](#)]
8. Chichkov, B.N.; Momma, C.; Nolte, S.; Von Alvensleben, F.; Tünnermann, A. Femtosecond, picosecond and nanosecond laser ablation of solids. *Appl. Phys. A Mater. Sci. Proc.* **1996**, *63*, 109–155. [[CrossRef](#)]
9. Stuart, B.C.; Feit, M.D.; Herman, S.; Rubenchik, A.M.; Shore, B.W.; Perry, M.D. Optical ablation by high-power short-pulse lasers. *JOSA B Opt. Phys.* **1996**, *13*, 459–468. [[CrossRef](#)]
10. Stancalie, A.; Ciobanu, S.S.; Sporea, D. Investigation of the effect of laser parameters on the target, plume and plasma behavior during and after laser-solid interaction. *Appl. Surf. Sci.* **2017**, *417*, 124–129. [[CrossRef](#)]
11. Egorov, R.I.; Strizhak, P.A. The light-induced gasification of waste-derived fuel. *Fuel* **2017**, *197*, 28–30. [[CrossRef](#)]
12. Zaitsev, A.S.; Egorov, R.I.; Strizhak, P.A. Light-induced gasification of the coal-processing waste: Possible products and regimes. *Fuel* **2018**, *212*, 347–352. [[CrossRef](#)]
13. Slyusarskiy, K.V.; Larionov, K.B.; Osipov, V.I.; Yankovsky, S.A.; Gubin, V.E.; Gromov, A.A. Non-isothermal kinetic study of bituminous coal and lignite conversion in air and in argon/air mixtures. *Fuel* **2017**, *191*, 383–392. [[CrossRef](#)]
14. Bhargava, S.K.; Tardio, J.; Prasad, J.; Föger, K.; Akolekar, D.B.; Grocott, S.C. Wet oxidation and catalytic wet oxidation. *Ind. Eng. Chem. Res.* **2017**, *45*, 1221–1258. [[CrossRef](#)]
15. Sazhin, S.S. Modelling of fuel droplet heating and evaporation: Recent results and unsolved problems. *Fuel* **2017**, *196*, 69–101. [[CrossRef](#)]
16. Lishtvan, I.I.; Falyushin, P.L.; Smolyachkova, E.A.; Kovrik, S.I. Fuel suspensions based on fuel oil, peat, waste wood, and charcoal. *Solid Fuel Chem.* **2009**, *43*, 1–4. [[CrossRef](#)]
17. Iegorov, R.I.; Strizhak, P.A.; Chernetskiy, M.Y. The review of ignition and combustion processes for water-coal fuels. In Proceedings of the European Physical Journal Conferences, Tomsk, Russia, 13–15 October 2015. [[CrossRef](#)]
18. Kuznetsov, G.V.; Feoktistov, D.V.; Orlova, E.G. Regimes of Spreading of a Water Droplet Over Substrates with Varying Wettability. *J. Eng. Phys. Thermophys.* **2016**, *89*, 317–322. [[CrossRef](#)]
19. Zahiri, B.; Sow, P.K.; Kung, C.H.; Mérida, W. Understanding the wettability of rough surfaces using simultaneous optical and electrochemical analysis of sessile droplets. *J. Colloid Interface Sci.* **2017**, *501*, 34–44. [[CrossRef](#)] [[PubMed](#)]
20. Damiani, D.; Meillot, E.; Tarlet, D. A Particle-tracking-velocimetry (PTV) investigation of liquid injection in a dc plasma jet. *J. Therm. Spray Technol.* **2014**, *23*, 340–353. [[CrossRef](#)]
21. Hadad, T.; Gurka, R. Effects of particle size, concentration and surface coating on turbulent flow properties obtained using PIV/PTV. *Exp. Therm. Fluid Sci.* **2013**, *45*, 203–212. [[CrossRef](#)]
22. Murastov, G.; Tsipilev, V.; Ovchinnikov, V.; Yakovlev, A. About laser heat absorbing impurities in the transparence matrix of pentaerythritol tetranitrate. *J. Phys. Conf. Ser.* **2017**, *830*. [[CrossRef](#)]
23. Burkina, R.S.; Morozova, E.Y.; Tsipilev, V.P. Initiation of a reactive material by a radiation beam absorbed by optical heterogeneities of the material. *Combust. Explos. Shock Waves* **2011**, *47*, 581–590. [[CrossRef](#)]
24. Valiullin, T.R.; Strizhak, P.A.; Shevyrev S.A. Low temperature combustion of organic coal-water fuel droplets containing petrochemicals while soaring in a combustion chamber model. *Therm. Sci.* **2017**, *21*, 1057–1066. [[CrossRef](#)]
25. Valiullin, T.R.; Strizhak P.A. Influence of the shape of soaring particle based on coal-water slurry containing petrochemicals on ignition characteristics. *Therm. Sci.* **2017**, *21*, 1399–1408. [[CrossRef](#)]
26. Volkov, R.S.; Kuznetsov, G.V.; Strizhak, P.A. Influence of droplet concentration on evaporation in a high-temperature gas. *Int. J. Heat Mass Transf.* **2016**, *96*, 20–28. [[CrossRef](#)]
27. Young, C.N.; Johnson, D.A.; Weckman, E.J. A model-based validation framework for PIV and PTV. *Exp. Fluids* **2004**, *36*, 23–35. [[CrossRef](#)]

